PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
B65D 85/50, C12C 3/04, A23K 3/02, B65D 30/02, 33/01, B32B 3/10, 3/26

A1

(11) International Publication Number: **WO 97/30911**

(43) International Publication Date: 28 August 1997 (28.08.97)

(21) International Application Number: PCT/US96/02254

(22) International Filing Date: 20 February 1996 (20.02.96)

(71) Applicants *(for all designated States except US)*: BEN-TZUR, Israel [US/IL]; 75 Snir Road, 25147 Kfar Vradim (IL). STEPAC L.A., THE STERILIZING PACKAGING COMPANY OF L.A., LTD. [IL/IL]; Building #12, Tefen Industrial Park, Tefen, 24959 Western Galilee (IL). STATE OF ISRAEL - MINISTRY OF AGRICULTURE [IL/IL]; Agricultural Research Organization, The Volcani Center, 50250 Bet Dagan (IL).

(72) Inventors; and

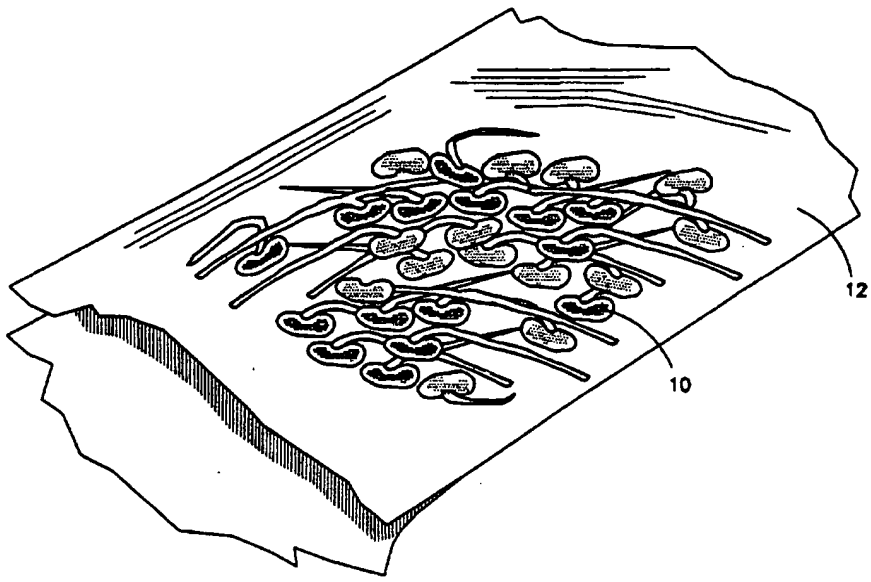
(75) Inventors/Applicants *(for US only)*: MARX NIR, Moira [IL/IL]; Moreshet-Garin Tikva, D.N. Misgav (IL). NEHORAY, Nery [IL/IL]; 30053 Kibbutz Gingar (IL). AHARONI, Nehemia [IL/IL]; 5 Hayasmin Street, P.O. Box 37, 76804 Mazkeret Batya (IL).

(74) Agents: GALLOWAY, Peter, D.; Ladas & Parry, 26 West 61st Street, New York, NY 10023 (US) et al.

(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: PLASTIC PACKAGING MATERIAL



(57) Abstract

This invention discloses a method of preserving horticultural products (10) by providing a plastic packaging material (12) having a thickness of up to about 500 microns and a permeability to water vapor exceeding about 1.5g mm/m^{-2} per day at 38 degrees C and 85 - 95 % relative humidity, whereby when the material (12) is used to package produce and other horticultural products (10) no condensation appears on a surface of the material.

PLASTIC PACKAGING MATERIAL

FIELD OF THE INVENTION

The present invention relates to plastic packaging materials generally and more particularly plastic packaging materials for food and horticultural products such as produce, as well as packaging techniques and packaged products.

BACKGROUND OF THE INVENTION

A great variety of plastic packaging materials is known in the patent literature. The following patents and published patent applications are thought to be representative of the state of the art, particularly in the field of nylon-6 packaging materials, packaging for produce and control of humidity in packaging:

U.S. Patents: 5,037,459; 4,842,741; 3,876,738

Japanese Abstracts: 05-329,947; 06-071,766; 05-316,943; 01-148,144; 57-167,331; 01-167062; 03-059,196; 06-062,728; 04-074,529; 01-309,621; 05-230,235

European Patents: 358,038; 566,097

WO Published PCT Application 8,404,529; 9,302,130

Australian Patent 636,284

SUMMARY OF THE INVENTION

The present invention seeks to provide an improved plastic packaging material which has a relatively high permeability to water vapor.

There is thus provided in accordance with a preferred embodiment of the present invention a plastic packaging material having a thickness of up to about 500 microns and a permeability to water vapor exceeding about 1.5g mm m^{-2} per day at 38 degree C and 85 - 90% relative humidity. The material allows for minimal or no condensation on its surface when used to package produce or flowers.

There is also provided in accordance with a preferred embodiment of the present invention a packaged produce product including a plastic packaging material having a relatively high permeability to water vapor and providing an atmosphere for the packaged produce which comprises approximately 4 - 12% O_2, 2 - 20% CO_2, and has a relative humidity of 85 - 100%.

There is additionally provided in accordance with a preferred embodiment of the present invention a method of preserving food products comprising:

providing a plastic packaging material of the type described hereinabove; and

at least partially enclosing the food product using the plastic packaging material, thereby to provide an environment for the food product which comprises approximately 4 - 12% O_2, 2 - 20% CO_2, and has a relative humidity of 85 - 100%.

Preferably, the plastic packaging material is based on a polyamide such as nylon-6 or nylon-66. For example, the material may be manufactured from a polymeric material that comprises a blend of nylon-6 or nylon-66 with other polymeric and/or non-polymeric components.

In accordance with a preferred embodiment of

the present invention, the raw material may be manipulated to increase the O_2 and CO_2 permeability of the film. For example, blends of nylon-6 and other components may be manufactured into a material having a porous character. Additionally or alternatively, the plastic packaging material may be manipulated after the film is formed. Thus the plastic packaging material may be perforated to have holes of approximately 1 - 10 mm diameter covering up to about 0.5% of the surface area of the material, or the plastic packaging material may be microperforated to have holes of approximately 0.05 - 1 mm diameter in a density of up to about 2000 holes per square meter of the material.

Microperforation or perforation may take place either in a continuous or in a batch process. For example, the perforation may be effected by contacting the material with one or more rollers, plates or other devices studded with appropriately sized and positioned pins or needles. Alternatively, the perforation or microperforation may be effected by use of laser technology. Perforation may occur during extrusion of the material downstream of a bubble collapsing frame or in tandem with a subsequent processing step such as printing or package forming.

In accordance with a preferred embodiment of the present invention, the raw material may be manipulated to tailor its permeability to water vapor. For example, blends of nylon-6 and other raw materials may be processed to produce a film with a lower water vapor permeability than a film processed from nylon-6 alone.

Additionally or alternatively, the packaging material may be manipulated by heat treatment or orientation processes to reduce its water vapor permeability.

In accordance with a preferred embodiment of the present invention, the raw material may be manipulated to absorb or degrade ethylene gas. For example, blends

of polyamides with other compounds which absorb or degrade ethylene may be employed in the manufacture of the packaging material.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be understood and appreciated more fully from the following detailed description, taken in conjunction with the drawing in which:

Fig. 1 is a simplified illustration of produce packaging in accordance with a preferred embodiment of the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Reference is now made to Fig. 1, which illustrates produce packaging in accordance with a preferred embodiment of the present invention. In the illustrated embodiment, produce 10, such as bean sprouts, is enclosed within a bag 12 preferably composed of nylon-6 or a blend containing nylon-6. Alternatively a package or wrap other than a bag may be provided. The nylon-6 film may be extrusion blown or produced in any other conventional manner from raw materials which are commercially available, inter alia, under the trade name Capron 8209 from Allied Signal or under the trade name Ultramid B4 from BASF.

In accordance with a preferred embodiment of the present invention the nylon-6 material may be extrusion blended with nylon-6I/6T (for example SELAR PA 3426 commercially available from Dupont) to produce films of 20 and 30 micron thickness. The ratios may be between 80 - 99% nylon-6 and 1 - 20% nylon-6I/6T. The resulting films have reduced water vapor permeability relative to nylon-6 alone and retain the ability to minimize condensation.

Additionally in accordance with a preferred embodiment of the present invention the material may be a blend of nylon-6 and polyolefins and compatibilizers (for example Orgalloy LE 6000, commercially available from Elf Atochem). Such blends can be employed to produce films having reduced water vapor permeability relative to that of nylon-6 alone and are characterized by minimal moisture condensation on the film surface when used to package produce or other horticultural products.

Further in accordance with a preferred embodiment of the present invention the nylon-6 material may be extrusion blended with nylon-11 or nylon-12 to produce films having reduced water vapor permeability relative

to that of nylon-6 alone and are characterized by minimal moisture condensation on the film surface when used to package produce or other horticultural products.

Additionally in accordance with a preferred embodiment of the present invention the polyamide material may be extrusion blended with porous additives, such as silica or diatomaceous earth to produce films having reduced water vapor permeability relative to that of polyamide alone and are characterized by ethylene sorption and by minimal moisture condensation on the film surface when used to package produce or other horticultural products. The ratios may be between 88 - 99% polyamide and 0.5 - 12% porous additive.

Additionally in accordance with a preferred embodiment of the present invention, the films may be oriented during manufacture or in a subsequent processing step to provide films having reduced water vapor permeability relative to unoriented films produced of the same raw materials. The oriented material is characterized by minimal moisture condensation on the material surface when used to package produce or other horticultural products.

Further in accordance with a preferred embodiment of the invention, films of polyamide with or without the above described additives and compositions and having thicknesses of 5 - 100 microns may be passed through a heating tunnel to heat the film to temperatures of 100 - 200 degrees centigrade to provide films having reduced water permeability relative to polyamide that is not heat-treated and are characterized by minimal moisture condensation on the film surface when used to package produce or other horticultural products.

Additionally in accordance with a preferred embodiment of the present invention a polyamide material may be extrusion blended with soluble starch or salt additives and then passed through a water bath at 4 - 100

degree C to extract the soluble additive in order to produce films having increased O_2 and CO_2 permeability relative to the base polyamide alone. The ratios may be between 88 - 99% polyamide and 1 - 12% soluble starch or salt additive. The bath water preferably is circulated, filtered and reintroduced to the bath on a continuous basis. Excess water is preferably removed from the film by passing it through a heating tunnel as described in the preceding paragraph.

Trays, baskets, containers, holders, bags, films or any other packaging material formed from films having a thickness generally in excess of 100 micron of nylon-6 or any other suitable polymer having water permeability exceeding 1.5 g mm m^{-2} per day at 38 degrees C with or without the additives or compositions described above may be provided by extrusion or any other suitable manufacturing process.

Film and sheets manufactured from any of the materials listed above and/or by any of the techniques listed above may be unperforated, or they may be perforated or microperforated to increase the permeability of the film to O_2 and CO_2.

For the purposes of the specification and claims, perforation refers to holes of approximately 1 - 10 mm diameter covering up to about 0.5% of the surface area of the material.

For the purposes of the specification and claims, microperforation refers to holes of approximately 0.05 - 1 mm diameter in a density of up to about 2000 holes per square meter of the material.

Reference is now made to the following examples which provide an indication of the scope of the present invention.

EXAMPLE I

Nylon-6 extrusion blown film having a thickness

of 40 microns was employed to package bean sprouts, mushroom, tarragon, chive and chickory lettuce. After 8 days of storage at 4 degrees C and a relative humidity of 90 - 97%, the sprouts were inspected and their weight loss was measured and compared with a control package of sprouts which had been stored under identical conditions in PVC film packaging.

The weight loss of the nylon-6 packaged sprouts was found to be less than of the control packaged sprouts. The nylon-6 packaged sprouts had a white color and were crisp, while the PVC packaged sprouts were brown and were not crisp.

The mushrooms were white and fresh after 18 days of storage in nylon-6 packaging. Visual observations of the tarragon, chive and chickory lettuce indicated that they stayed fresher longer in the nylon-6 packaging as compared to polyethylene packaging.

EXAMPLE II

Nylon-6 extrusion blown film having a thickness of 20 microns and perforations 6 - 8 mm in diameter was used to package grapes. After 12 days of storage at 0 degrees C and 7 days storage at 20 degrees C, the condition of the grapes was compared with control packages packaged in both perforated and non-perforated polyethylene. The grapes packaged in nylon-6 showed a higher percentage of healthy clusters and lower levels of decay than the control packages.

EXAMPLE III

Nylon-6 extrusion blown film having a thickness of 20 microns and microperforations 0.8 mm in diameter was used to package snap beans (green beans). After 5 days of storage at 5 degrees C and 3 days storage at 20 degrees C, the condition of the beans was compared with control packages packaged in micro-perforated polyethylene. The beans packaged in nylon-6 showed less weight loss, less rusty spots and substantially no mold growth

as compared with the control packages.

EXAMPLE IV

Nylon-6 extrusion blown film having a thickness of 20 microns in both perforated and microperforated forms was used to package cucumbers. After 6 days of storage at 8 degrees C and 3 days storage at 20 degrees C, the condition of the cucumbers was evaluated and was found to be very good. The cucumbers packed in microperforated packages showed no chilling injury, while those in perforated packages showed very low chilling injury.

EXAMPLE V

A blend of 20% nylon 6I/6T and 80% nylon-6 was extrusion blown into a film 20 microns thick, microperforated, and used to package cherry tomatoes. After a number of days, there was no condensation in the packages and the tomato quality was better than that of tomatoes packaged in alternative materials.

EXAMPLE VI

A blend of 10% nylon 6I/6T and 90% nylon-6 was extrusion blown into a film 30 microns thick, perforated, and used to package lettuce.

EXAMPLE VII

25 micron thick nylon-6 film, manufactured by a chill-roll cast process and then biaxially oriented by means of tenter frame orientation equipment was used to wrap cut flowers.

EXAMPLE VIII

30 micron thick nylon-66 film, manufactured by an extrusion blown film process, was perforated and then passed through a heating tunnel at 200 degrees C and was used to package carrots.

EXAMPLE IX

15 micron thick nylon-12 film, manufactured by extrusion in a chill-roll cast process and microperforated was used to package berries.

EXAMPLE X

A copolymer of nylon-6 and nylon-66 is extruded into a film 20 microns thick via a blown film double-bubble process that imparts a high degree of orientation to the film. The film is then microperforated and used to package lettuce.

EXAMPLE XI

A blend of nylon 610 and 8% soluble starch is extruded into a 30 micron thick film by a water quench cast film process. The soluble starch is extracted during the water quenching stage, leaving a porous film which is then passed through a heating tunnel and ultimately used to package green and red peppers.

EXAMPLE XII

A blend of 95% nylon-1 and 5% nylon 6I/6T is extruded in a chill-roll cast process to produce a sheet 150 microns thick. This material is then perforated and thermoformed into trays to package corn.

It will be appreciated by persons skilled in the art that the present invention is not limited by what has been particularly shown and described hereinabove. Rather the scope of the invention is defined only by the claims which follow:

C L A I M S

1. A plastic packaging material having a thickness of up to about 500 microns and a permeability to water vapor exceeding about 1.5g mm m^{-2} per day at 38 degree C and 85 - 90% relative humidity, whereby when the material is used to package produce and other horticultural products no condensation or minimal condensation appears on a surface of the material.

2. A packaging material according to claim 1 and wherein the plastic packaging material is based on a polyamide formulation.

3. A packaging material according to claim 1 or claim 2 and wherein the plastic packaging material is perforated to have holes of approximately 1 - 10 mm diameter covering up to about 0.5% of the surface area of the material.

4. A packaging material according to any of the preceding claims and wherein said plastic packaging material is microperforated to have holes of approximately 0.05 - 1 mm diameter in a density of up to about 2000 holes per square meter of the material.

5. A packaged produce product including a plastic packaging material having a relatively high permeability to water vapor, and that allows the package produce to be contained in an atmosphere which comprises approximately 4 - 12% O_2, 2 - 20% CO_2, and has a relative humidity of 85 - 100%, whereby no condensation or minimal condensation appears on a surface of the material.

6. A packaged product according to claim 5 and wherein the plastic packaging material is based on a

polyamide formulation.

7. A packaged product according to claim 5 or claim 6 and wherein the plastic packaging material is perforated to have holes of approximately 1 - 10 mm diameter covering up to about 0.5% of the surface area of the material.

8. A packaged product according to any of the preceding claims 5 - 7 and wherein said plastic packaging material is microperforated to have holes of approximately 0.05 - 1 mm diameter in a density of up to about 2000 holes per square meter of the material.

9. A packaged product according to any of claims 5 - 8 and wherein said product comprises horticultural products.

10. A method of preserving horticultural products comprising:

providing a plastic packaging material of the type described hereinabove; and

at least partially enclosing the horticultural product using the plastic packaging material, thereby to provide an environment for the horticultural product which comprises approximately 4 - 12% O_2, 2 - 20% CO_2, and has a relative humidity of 85 - 100%.

11. A method according to claim 10 and wherein the plastic packaging material is based on a polyamide formulation.

12. A method according to claim 10 or claim 11 and wherein the plastic packaging material is perforated to have holes of approximately 1 - 10 mm diameter covering

up to about 0.5% of the surface area of the material.

13. A method according to any of the preceding claims 10 - 12 and wherein said plastic packaging material is microperforated to have holes of approximately 0.05 - 1 mm diameter in a density of up to about 2000 holes per square meter of the material.

14. A method according to any of claims 10 - 13 and wherein said product comprises horticultural products.

15. A method according to claim 12 or claim 13 and wherein the perforation takes place in a continuous process.

16. A method according to claim 12 or claim 13 and wherein the perforation takes place in a batch process.

17. A method according to any of claims 12, 13, 15 and 16 and wherein perforation occurs during extrusion of the material.

18. A method according to any of claims 12, 13, 15 and 16 and wherein perforation occurs during a subsequent processing step.

1/1

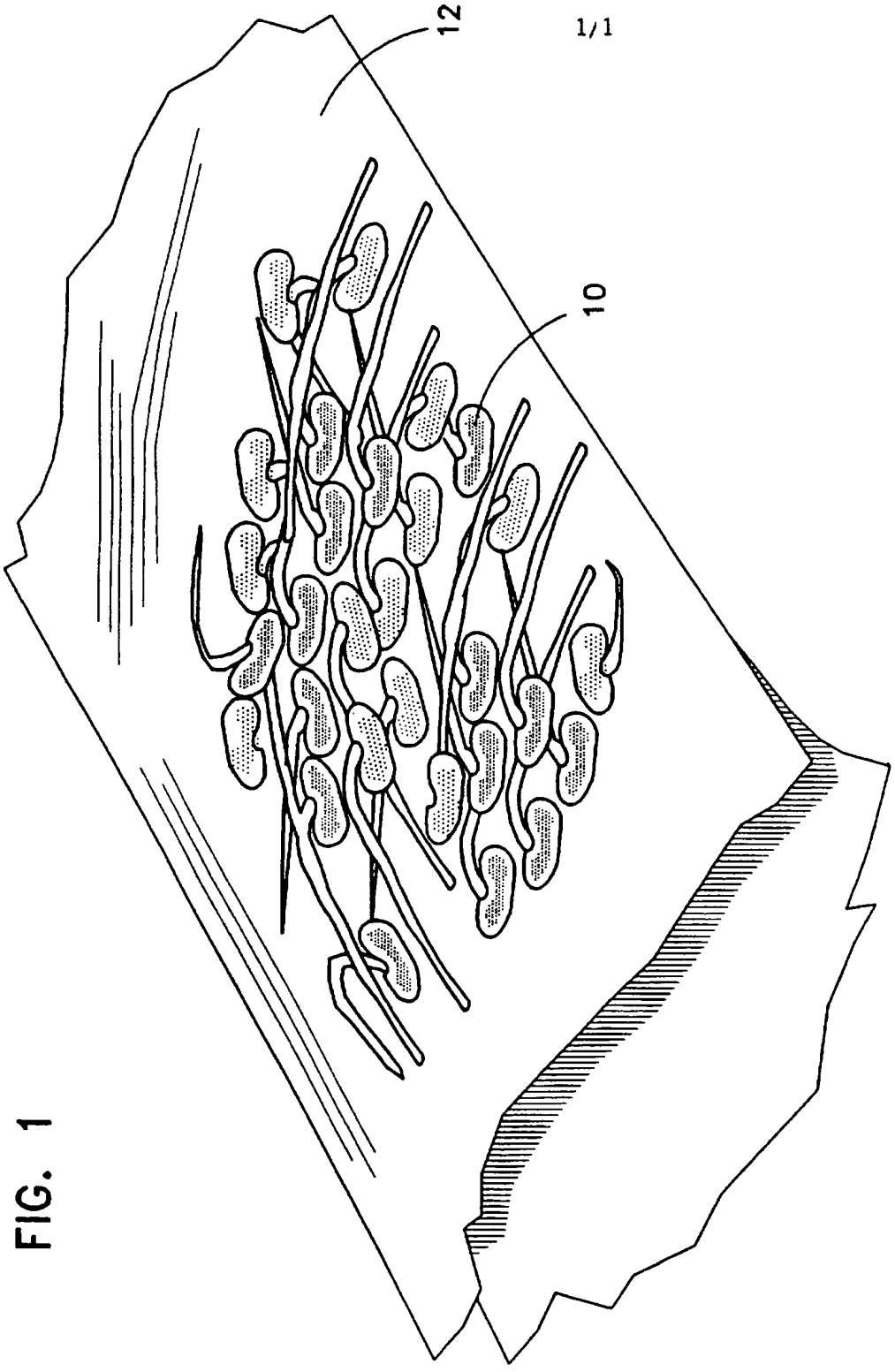


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/02254

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :Please See Extra Sheet.
US CL : 426/118, 415, 419; 428/35.2, 35.5, 131, 315.7
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 426/118, 415, 419; 428/35.2, 35.5, 131, 315.7

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, A, 5-329947 (DIANIPPON PRINTING CO LTD) 14 December 1993, English Abstract.	1-3, 5-7, 10-12
Y	JP, A, 5-230235 (SUMITOMO BAKELITE CO) 07 September 1993, English Abstract.	1-3, 5-7, 10-12
Y	US, A, 5,492,705 (PORCHIA ET AL) 20 February 1996, col. 2, line 43 - col.3, line 28.	1-3, 5-7, 10-12
A	EP, A, 0,538,713 (KAGAWA ET AL) 28 April 1993.	
A	US, A, 5,405,561 (DAIS ET AL) 11 April 1995.	
A	US, A, 3,682,028 (CLAYTON ET AL) 08 August 1972.	

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 21 MAY 1996	Date of mailing of the international search report 08 JUL 1996
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer CHRISTOS S. KYRIAKOU Telephone No. (703) 308-2351

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/02254

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4, 8, 9, and 13-18
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/02254

A. CLASSIFICATION OF SUBJECT MATTER:
IPC (6):

B65D 85/50; C12C 3/04; A23K 3/02; B65D 30/02, 33/01; B32B 3/10, 3/26